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Pulsed-laser Polymerization (PLP) of N-isopropyl Acrylamide (NIPAM) in Water: a Qualitative Study

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SUMMARY : Pulsed-laser polymerization results are presented for N-isopropyl acrylamide (NIPAM) in water; the data show the overtones that satisfy one of the PLP consistency tests. Apparent propagation rate coefficients $k_{p,app}$ were measured; these decrease with increasing concentrations of initiator, monomer and polymer, sugeestina significant association between the various species involved. The PLP data also qualitatively show the presence of low rates of termination and transfer.

Introduction

Pulsed-laser polymerization is acknowledged as the method of choice to measure propagation rate coefficients (k_p) in free-radical polymerization(1-2) with critically-evaluated data for methacrylates, styrene, acrylates and other monomers now available (e.g. (3-4)). The method is especially useful because it provides internal consistency tests: e.g., the same apparent value of k_p for different "overtones" (chains which are terminated by successive pulses). However, problems have been encountered in certain cases: i) monomers with very high k_p (typically acrylates); ii) when high transfer activity (to monomer, polymer ancl/or solvent) increases the non-controlled termination; iii) monomers exhibiting high or low termination rate coefficients, enhancing the background molecular weight distribution (MWD). These drawbacks may sometimes be avoided by respectively i) and ii) lowering the temperature and/or increasing the frequency of the laser,(5) and iii) changing the number of radicals created per pulse (laser energy or initiator concentration).

Few results have been published applying the technique to water-soluble monomers,(6,7) and some of the early data[7] were obtained before the need for the consistency tests was recognized. Those early results, for (meth)acrylamide derivatives, showed unusual variation of k_p with temperature,

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which were interpreted as arising from dimerization and/or complexation (it is however emphasized that these data were not checked for PLP consistency). This present note focuses on the many difficulties experienced with PLP for a water-soluble monomer and polymer, N-*iso*-propyl acrylamide. Some difficulties in the GPC characterization and the effect of PLP conditions on k_p measurements are presented.

GPC characterization

A crucial parameter in the determination of k_p is the measurement of the absolute molecular weight distribution (MWD). In PLP, the first inflection point of the MWD L_O corresponds to the molecular weight of the polymer formed during a time τ separating two pulses, and L_i to termination in subsequent pulses, so that:

$$L_{0,i} = i\, k_p\, [\mathrm{M}]\, \tau$$

where i = 1,2,3 ... and [M] the monomer concentration (taken as constant when the polymerization is carried out at low conversion).

Poly(NIPAM) samples for GPC calibration ranging between $2.5\mathrm{x}10^3$ and $3\mathrm{x}10^5$ were prepared using the living free-radical process called radical addition fragmentation transfer polymerization (RAFT).[8,9] The controlled molecular weight and very low polydispersity of the polymer were confirmed by MALDI analyses of two samples.

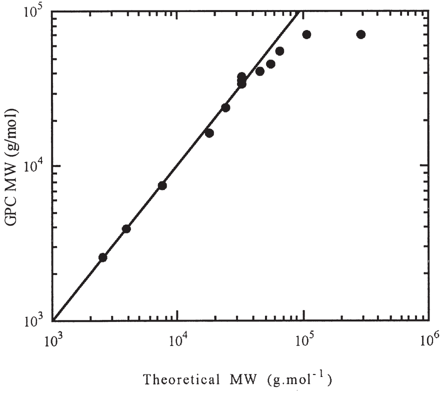

Fig. 1. Theoretical MW (calculated according to the amount of transfer agent introduced into the RAFT polymerization) versus MW obtained by GPC in THF (using a polystyrene calibration curve) for poly(NIPAM) samples synthesized by RAFT.

A comparison between the calculated and GPC apparent molecular weight (using a polystyrene calibration) is given in Figure 1. The straight line shows the domain where the Mark Houwink parameters were determined and the PLP experiments performed, i.e. MW < $5\text{x}10^4$. Using the classical Mark Houwink parameters for styrene (K = $11.2\text{x}10^{-3}$ mL g^{-1} and a = 0.7 1), the values found here for the poly(NIPAM) (K = 25.4x 10^{-3} mL g^{-1} and a = 0.62) are close to those given in the literature (K= 9.6 10^{-3} mL g^{-1} and a = 0.65).$^{10)}$

It has been noted that poly(NIPAM) MWDs obtained by GPC in THF are in many cases far less than those reported using other methods, such as viscometry or light scattering.$^{11-12)}$ This discrepancy was also seen in the present study, and could be due to presence of microgels made up of high polymer chains, exhibiting a hydrodynamic volume independent of the polymer MW.

PLP measurements

PLP samples were obtained using uranyl nitrate as photoinitiator and a laser frequency of 30 Hz. As shown in Figure 2, points of inflection corresponding i = 1 and to higher overtones in eq 1 are clearly seen. The second overtones give a point of inflection very close to twice that of the first, thereby fulfilling one of the PLP consistency tests.

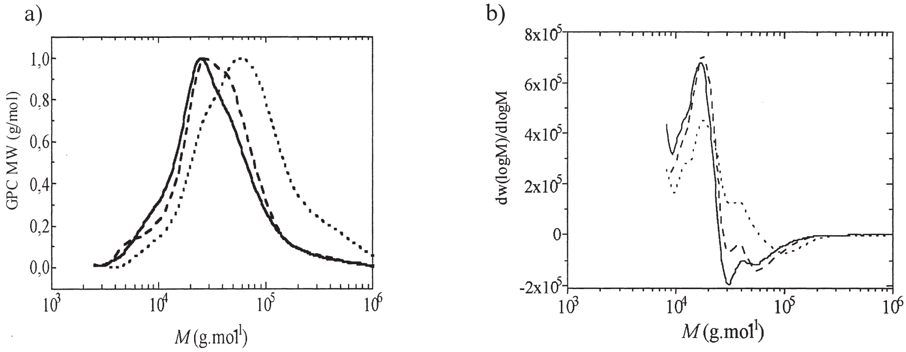

Fig. 2: Influence of the initiator concentration on the PLP traces. a) GPC distributions; b) derivatives of GPC distributions. $[U0_2(N0_3)_2]$ = 10^{-3} mol L^{-1} (...); 5 10^{-3} mol L^{-1} (---); 10^{-2} mol L^{-1} (-). PLP conditions: [NIPAM] = 0.4 mol L^{-1}; temperature = 10°C; number of pulses = 200; energy per pulse = 30 mJ.

Termination

The PLP traces give some information. about the effects of termination. The sample with the lowest initiator concentration displays a GPC distribution that is unexpected for PLP conditions, which otherwise should be a primary peak (chains formed between two pulses) and a shoulder (polymer formed during two dark times). Increasing the amount of chains terminated between the two pulses rather than at each pulse induced a "background" distribution. This latter induces a distortion of the MWD that can sometimes hide the PLP distribution. In the present case, it is postulated that with low radical flux, the termination rate is so low that very few chains are terminated at each laser pulse; increasing the initiator increases the termination rate givinc, a more normal PLP GPC distribution.

Transfer

Transfer reactions, either to monomer or polymer, can affect PLP GPC distributions. Figure 3 shows the influence of the temperature on the GPC profiles, obtained under high radical flux conditions.

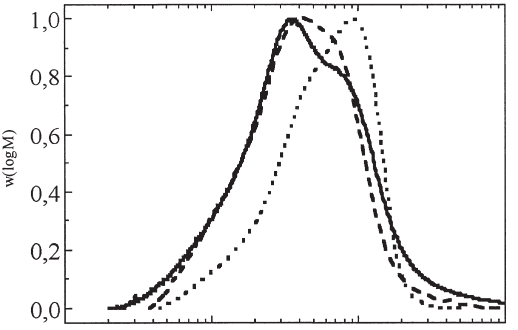

Fig. 3: Influence of the temperature on the PLP traces. T = 4.8 °C (—); 17.5 °C (---). PLP conditions: [NIPAM] = 0.4 mol L^{-1}; [$UO_2(NO_3)_2$] = 10^{-3} mol L^{-1}; number of pulses = 200; energy per pulse = 14.4 mJ.

The same trends are observed as seen with initiator concentration. Typically, increasing the temperature increases the rate coefficients of side reactions such as transfer, and increases the background MWD. However, apparent values of k_p were seen to level off for temperatures of 17°C and above, as shown in Figure 4. That means that, though the first and second inflection points are still observed, the apparent values of k_p cannot be the actual k_p.

The ratio $r = L_0/L_1$, shown in Figure 4, decreases with temperature, emphasizing these discrepancies. One problem arises from the overlap of the first inflection point by the background MWD. The second inflection point when available provides a better estimate of k_p.

Propagation

Table 1 gives the variation of $k_{p,app}$ with the concentrations of monomer and initiator. A striking decrease of $k_{p,app}$ with solute concentration is observed. The variation of $k_{p,app}$ with initiator concentration is even stronger. It is seen in Figure 2b that the inflection point, and thus $k_{p,app}$, varies with initiator concentration. However, experiments conducted with another initiator, 2,2'-azobis (2-amidino propane) dihydrochloride (V50), showed the same trend, though exhibiting a "classical" PLP GPC trace. These variations cannot therefore be the result of transfer reactions. These variations may however arise from effects of solvation of both monomer and polymer, depending on their concentration in solution. The formation of dimers and/or complexes with increasing solute concentration would decrease $k_{p,app}$. The solvent effect was moreover seen to be very strong in water: extrapolation of the data (Table 1, column 2) to zero and infinite dilution gives $k_{p,app}$ values from 1×10^4 to 7×10^4 $dm^3\ mol^{-1}\ s^{-1}$, respectively.

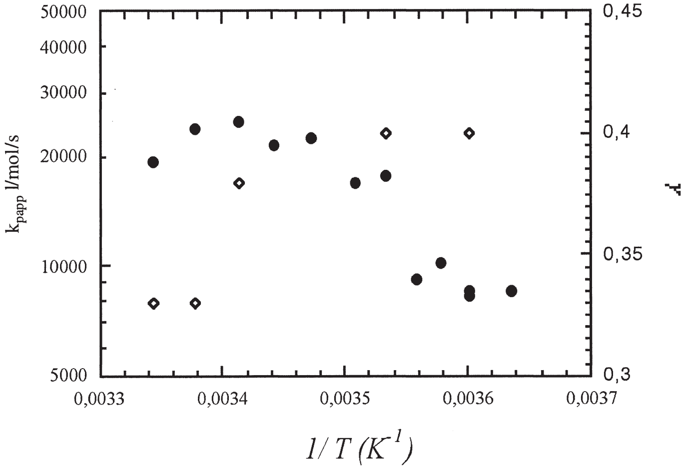

Fig. 4: Evolution of $k_{p,app}$ (•) and r (◇) with the inverse temperature. PLP conditions: [NIPAM] = 0.8 mol L-I; $[UO_2(NO_3)_2]$ = 10^{-2} mol L^{-1}; number of pulses = 200; energy per pulse 14.4 mJ.

Table 1: Influence of the solute concentrations on $k_{p,app}$. Each value is the average of at least two measurements. PLP conditions: temperature = 10°C; number of pulses = 200; energy per pulse = 30 mJ.

$[M]^{a)}$ $(mol.L^{-1})$	$k_{p,app}$ $(L.mol^{-1}.s^{-1})$	[Initiator] $(mol.L^{-1})$	$k_{p,app}$ $(L.mol^{-1}.s^{-1})$
0.08	37900	0.002	28100
0.20	24200	0.005	25500
0.32	21800	0.01	21800
0.40	17300	0.03	20500

a) [Initiator] = 0.01 mol.L-'; b) [M] = 0.32 mol.L-1.

Conclusions

This study shows that association and/or association (complexation) have a strong effect on the apparent propagation rate coefficient in NIPAM, and also shows the importance of choosing PLP conditions. GPC traces from PLP may depend on monomer and polymer properties such as association, and can be corrected by judiciously changing the pulse number, initiator amount and concentration. However, strong solvent effects cannot be avoided in the

PLP study of the water-soluble monomer NIPAM and should be taken into account for designing the conditions of polymerization and the consequent kp,app measurement.

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